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DEPARTMENT OF The ARMY
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The constitution of atmospheric aerosol.

by C. Junge.

d. The change in the size of nuclei with relative humidity.

As is well known, the assumption that the nuclei represent droplets of solution which hold a vapor pressure equilibrium with the surrounding air, indicates a dependence of the nucleic size upon relative humidity. The vapor pressure of such a droplet of solution vis-a-vis a level water surface of the same temperature is changed by two factors: an elevation owing to curvature of the surface and a depression due to the dissolved substance. Considering the range of nucleic sizes of interest here, the influence of the electrical charge may be ignored.

$$ p/p_0 = 1 + \Delta p_{nucl\,r}/p_0 - \Delta p_{sol}/p_0 $$

p_0 = vapor pressure of the level, pure water surface;

p = vapor pressure at the surface of the solutional droplet.

If only particles above $r = 10^{-6}$ cm are considered,

$$ \Delta p_{nucl\,r}/p_0 = 2\alpha/RTr = C_1/r $$

α = surface tension; R = gas constant; T = absolute temperature.

and, for not too strongly concentrated solutions, according to Raoult's law:

$$ \Delta p_{sol}/p_0 = a \cdot n_1 / (n_0 + a\,n_1) $$

$a = 1 + \varepsilon\,(n_1 - 1)$; n = number of ions into which a molecule may disintegrate; ε = degree of dissociation; n_1 = mole of dissolved substance; n_0 = mole of the solvent.

If, as is customary, the magnitude $\Delta p_{sol}/p_0$ is designated as a function of r by the introduction of the droplet's volume, then, since $n_0 \cdot m_0 + n_1 \cdot m_1$ represents the total dimensions of the droplet,

$$\frac{\Delta p_{sol}}{\Delta p_0} = \frac{3 n_1 \cdot (n_0 \cdot m_0 + n_1 \cdot m_1)}{4 \cdot \pi \cdot r^3} \cdot \frac{\alpha}{(n_0 + a n_1) \cdot \varrho} = \frac{const}{r^3} f(conc.)$$

m_0 = molecular weight of the solvent; m_1 = molecular weight of the dissolved substance; ϱ = density of the solution.

f (concentration) is a constant only in the case of a small n_1, i.e. in diluted solutions, and may be written

$$\Delta p_{sol} / p_0 = C_2 / r^3.$$

This leads to the well-known expression for the relation between the relative vapor pressure of the nucleus and its radius

$$p/p_0 = 1 + C_1/r - C_2/r^3.$$

The theory of solutions was able initially to furnish a satisfactory qualitative explanation derived from visual observations, etc. concerning the growth of nuclei, especially since the problem of the condensational process proper, i.e. the growth of nuclei close to water vapor saturation (therefore with strongly dissolved solutions in the nuclei) were of interest. The errors perpetrated due to neglect in the derivation of the expression C_2/r^3 were not treated in the literature for this reason. However, if the growth curves of nuclei are to be calculated up to moderate and low humidity, the dependence of α, a and ϱ upon the concentration of the dissolved substance naturally must be considered. It is not surprising, therefore, if Dalal, for instance, fails to obtain a satisfactory agreement between the measurements of magnitudes of pure solutional droplets in dependence upon the relative humidity and the last listed simplified formula.

In precise calculations of such growth curves, the best line of departure is given by data found in chemico-physical tables as functions of the concentration. Unfortunately such data are complete only for a few substances (e.g. H_2SO_4, HNO_3). When such calculations with un-objectionable data still show deviations from observations, they may be attributed to the theory of the solutional nucleus, and would indicate that macroscopic laws may not be utilized without limitations within the range of the colloidal dimensions of nuclei.

A conclusion unjustifiably drawn from the solutional nucleus theory on the basis of the simplified formula was the independence of the growth curves from the type of dissolved nucleus. This shows a close approximation in the case of high humidity, but considerable deviation sets in at

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moderate humidity, since the functional correlation of the magnitudes $\varkappa$, a and η is dependent upon the specific properties of the substances. The character of the growth curves is barely affected thereby, their course is very similar, and only the absolute figures of nucleic growth differ more strongly, as would the ratio of radii at 95 and 40% relative humidity.

Such growth curves calculated with precise data, depicted initially by the nitric acid example for "potential radii" (i.e. radii at 100% relative humidity) 10^{-4}, 10^{-5} and 10^{-6} cm (Fig. 4). These curves differ essentially only above 90% humidity, since the growth of large particles is considerably stronger immediately below saturation, due to the weak influence of surface curvature. In order to find a measure for the extent of droplet growth which would indicate its behavior in the area of moderate humidity, the relation

$$W = \frac{\text{radius at 95\% humidity}}{\text{radius at 40\% humidity}}$$

is formed (growth value).

As table 4a shows, this value is identical for potential radii 10^{-4} and 10^{-5} and only decreases perceptibly at 10^{-6} cm.

Since the following investigations refer primarily to cruder aerosols, W is suited as a measure for the absolute amount of growth. The relative value of 40% humidity was chosen because in many observations no data is available for lower humidity, and comparison would thus be impossible.

Growth curves for various substances at the same potential radius of 10^{-5} are listed in Fig. 5. The process of crystallization is given for NaCl in the assumption that this had set in in the case of a saturated solution, and that a spherical aggregate of salt was left. The curves show a rather uniform growth in the humidity region below 80%, increasing above 80% with the approach of saturation. We have pointed out that this circumstance does not agree with the observations (which show practically no growth below 60-70% humidity), and that the concept according to which the natural aerosol consists predominantly of solutional droplets (27) requires correction. It was shown that a considerably more favorable qualitative agreement exists in the case of mixed droplets which contain a larger share of insoluble substance and therefore are subject to a very small alteration in size at humidity below 60%, where the solid nucleus is enveloped only by a thin solutional membrane. The growth of such mixed droplets is shown in Fig. 6, where the solid portion is assumed to be completely insoluble. The corresponding W-values in Table 4 naturally are considerably smaller than those of the solutional droplets.

1. Calculated values.

a) Pure nitric acid at different potential radii

Potential nucleic radius 10^{-4} cm $W = 1.80$
10^{-5} cm $= 1.80$
10^{-6} cm $= 1.54$

b) Various pure substances at a potential nucleic radius of 10^{-5} cm

HNO_3 $W = 1.80$ droplets cannot exist at normal humidity
H_2SO_4 $= 1.60$
$CaCl_2$ $= 1.70$
$NaCl$ $= 2.57$ with crystallization

c) Mixed nuclei H_2SO_4 – insoluble nucleus at a potential nucleic radius of 10^{-5} cm

Radius of the solid nucleus 0 cm $W = 1.60$
$3 \cdot 10^{-6}$ $= 1.47$
4 " $= 1.36$
5 " $= 1.25$
6 " $= 1.16$
7 " $= 1.12$
8 " $= 1.06$

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2. Observed values.

Aerosol			Nucleic radius	W	Remarks
Gas flame ions			ca. $7 \cdot 10^{-8}$ cm	1.28	According to (39)
Natural aerosol			$1 - 3 \cdot 10^{-4}$	1.27	Mean of 91 indiv. measurements of n.w/mixed character.
Natural aerosol			$1 - 13 \cdot 10^{-4}$	1.49	Mean of 17 indiv. measurements of n.w/irreg. growth curves
Mixed nuclei:					
$CaSO_4$: $CaCl_2$ =	2:1		$1.5 - 2.5 \cdot 10^{-4}$	1.28	
$CaSO_4$: $CaCl_2$ =	3.5:1		"	1.23	This aerosol corresponds to the mean of the natural aerosol with respect to its Z/V value
$CaSO_4$: $CaCl_2$ =	10:1		"	1.19	
$CaCl_2$: $NaCl$ =	1:1		$2.5 - 7.0 \cdot 10^{-4}$	1.70	
$NaCl$: $PbCl_2$ =	1:1		$4.0 - 7.0 \cdot 10^{-4}$	1.89	
$NaCl$: $PbCl_2$ =	1:1		$2.5 - 6.0 \cdot 10^{-6}$	1.60	

Table 4. The growth values of nuclei $W = \dfrac{\text{radius at } 95\% \text{ humidity}}{\text{radius at } 40\% \text{ humidity}}$ of diverse material composition.

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The assumption of an insoluble nucleus with an enveloping solution naturally represents a strong simplification of possibilities which may arise in the case of mixed nuclei. If the nucleus consists of a more or less easily soluble substance, the growth curves are subject to considerable modification. Fig. 7 shows such possibilities schematically, assuming variable solubility of the poorly soluble portion of the substance and variable conditions of mixture. The material properties of $CaCl_2$ were used as a basis, where a part of dissolved $CaCl_2$ is to have a different solubility, expressed by the different degrees of relative saturation humidity at 96%, 90%, etc. With increasing humidity, the solid nucleus goes progressively into solution, until it dissolves completely with the achievement of the saturation vapor pressure, and the particle grows rapidly in order to continue its growth on the curve of the pure solutional droplet. It is essential that these growth curves show differentiable growth in nuclei below and above 60-70% relative humidity, even more so than in the case of insoluble parts of the substance, unless solubility becomes very great or the share of the more poorly soluble substance is low.

In the presence of more than two substance components, the circumstances become more complicated, the growth curves may contain several variables, but will principally reveal the same picture. In this connection W may assume all values up to the upper limit of purely crystallizing substances (e.g. NaCl with 2.6). In the calculation of the curves in Fig. 7, which takes an elementary course, it is assumed as a foregone conclusion that no reciprocal chemical effect exists between the dissolved components. The resultant complex salt formations and similar processes associated with established compounds will naturally modify these conditions. It should be pointed out that crystallization (or dissolution) of a component is less vigorous and less pronounced in its volume change in connection with such mixed nuclei: Sudden alterations in size become more or less fluent transitions.

We must conclude from these considerations -- if the mixed nucleic nature of the natural aerosol is admitted -- that a mean growth curve of the entire aerosol must be distinguished from the character of the growth curve of an individual particle. In addition, mixed aerosols will always show a smaller average growth at lower humidity vis-a-vis pure solutional droplets of a hygroscopic substance. At the same time a gradual transition from droplets to solid particles must take place below 60-70% humidity. We shall see that this agrees with observations.

A few words about the concept of hygroscopicity. As Dalal (10) so correctly stresses, this concept is very vague; in addition to a substance's solubility it includes the capability of adsorption, absorption and capillary condensation. As long as a solution maintains a vapor pressure balance with the surrounding relative humidity and the solution is not as yet saturated, the hygroscopicity of a pure substance has no influence on the action of the solutional droplet. As we have seen, this behavior is determined solely by the dependence of the vapor pressure, the density, the degree of dissociation upon the solution's concentration. The delineation of this range toward low humidity is determined first of

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all by the unequivocal value of the saturation concentration (solubility). Desseus (8) showed that solutional droplets could in part be strongly supersaturated. On the other hand, substances show macroscopic differences in their ability to go into solution automatically from a dry state, in the event a solution can exist at the humidity in question. Thus the hygroscopicity of pure substances has a practical expression, as far as these two points are concerned, making it difficult to measure this concept quantitatively. Aside from this action, solubility remains the decisive property of a substance's hygroscopicity.

In the case of mixed nuclei, the concept of hygroscopicity takes on an entirely different sense. Here it could be defined as the nucleic content (perhaps in percentage of weight) of hygroscopic, i.e. in practice easily soluble substance, in addition to its content of poorly soluble or insoluble matter. This content dictates the entire action of the nucleus, especially its growth, and its W-value at the same time is a measure of its hygroscopicity.

Wall (28) has pointed out that below a potential radius of ca. 10^{-6} cm other reasons may be responsible for the growth of nuclei with humidity. Below this size the deposit of polymolecular water layers due to surface adsorption (as occurs in wettable substances such as glass) causes the same changes as those calculated in connection with solutional droplets. Thus a delineation of the processes of adsorption, dissolution and absorption becomes difficult in this range, and the borderlines between these phenomena become obliterated. In the evaluation of adsorption, the elevation in vapor pressure due to the curvature of the surfaces must be considered, allowing the macroscopically established adsorption layers of water to become apparent in small particles only at higher humidity.

As discussed elsewhere (27), the presence of gaseous traces may be significant in the growth of nuclei. There are as yet no observations recorded, since it is difficult to divorce gases and aerosols in the analysis for trace substances. Coste and Conitier (29) demonstrated in London and vicinity that the SO_2 content is considerably larger than the content of droplet-bound H_2SO_4 (ratio in the order of magnitude 100:1), and that in the main a parallel course was evident between the two components. Oxidized SO_2 requires aqueous surfaces for the formation of H_2SO_4, as found in aerosol. Evidently sulfuric acid is formed in the fog and is not its cause, as often assumed. The observations make it probable that no oxidation of SO_2 occurs in dry air, and that pure H_2SO_4 in liquid form is rare. There are as yet no data on other substances concerning the reciprocal effect between gas phase and aerosol.

On the whole, the gas phase of poorly volatile substances such as acids should not be underrated quantitatively. Above an acid of known concentration, e.g. HCl, there is a gas phase of H_2O and HCl vapor in equilibrium, even though the vapor pressure of the latter is low. It is nevertheless considerably higher than that corresponding to trace substances found in natural air. When the humidity is elevated, the balanced acid loses concentration and the vapor pressure of the acid must consequently abate. It is possible to demonstrate in this manner

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that pure droplets of HCl and HNO_3 can exist only at very high humidity, judging by the traces occurring in natural air. If the vapor pressures of HCl and HNO_3 listed in pertinent tabulations are used (in part after extrapolation to room temperature by means of August's vapor pressure formula), curves may be entered on a humidity – trace substance diagram, delineating areas in which pure acid droplets are possible. It is evident from Fig. 8 that droplets of HCl and HNO_3 can occur only directly below water vapor saturation, since the observed trace substances in the air are 20 γ/m^3 in size. The deposit of already present particles is not affected thereby, since they absorb such a portion of trace gas under all circumstances, until a solutional balance is achieved. The growth curves obtained thereby show a similarity with those given in Fig. 7 for mixed nuclei, if the solid portion possesses poor solubility (27).

The data on the (very low) partial vapor pressure of H_2SO_4 (partially dissociated in H_2O and SO_3) is so scanty that no precise specifications may be given. However, droplets of pure H_2SO_4 still seem possible above ca. 40% humidity in connection with traces of 1-10 γ/m^3.

It is probable that the acid molecules and other substances in their gas phase immediately take up a certain number of water molecules and thus become objects that are no longer molecules in the strict sense nor yet condensational nuclei of the magnitude discussed here. They are not counted in Aitken's nucleus counter, and the designation condensational nuclei is inappropriate for such particles (13) in view of the conditions governing natural aerosol.

It was silently postulated in all of the foregoing considerations that the macroscopically known laws remain valid also for the colloidal range of condensational nuclei. This is by no means certain a priori, and results introduced later also show deviations. Colloid chemistry requires increased solubility, e.g. for small particles; this is confirmed by observations, since the dissolution of pure salt particles, e.g. $NaCl$, usually occurs prior to the achievement of saturation pressure upon elevation of humidity, and in any case when that pressure is exceeded. Moreover, the internal pressure of several atmospheres caused in such small droplets by surface tension may alter the solubility. In this category belongs also the formation of strongly supersaturated solutions in droplets. If these phenomena are ignored, however, subsequently imparted observations show that the macroscopic laws of solutions indeed govern the behavior of aerosols in close approximation.
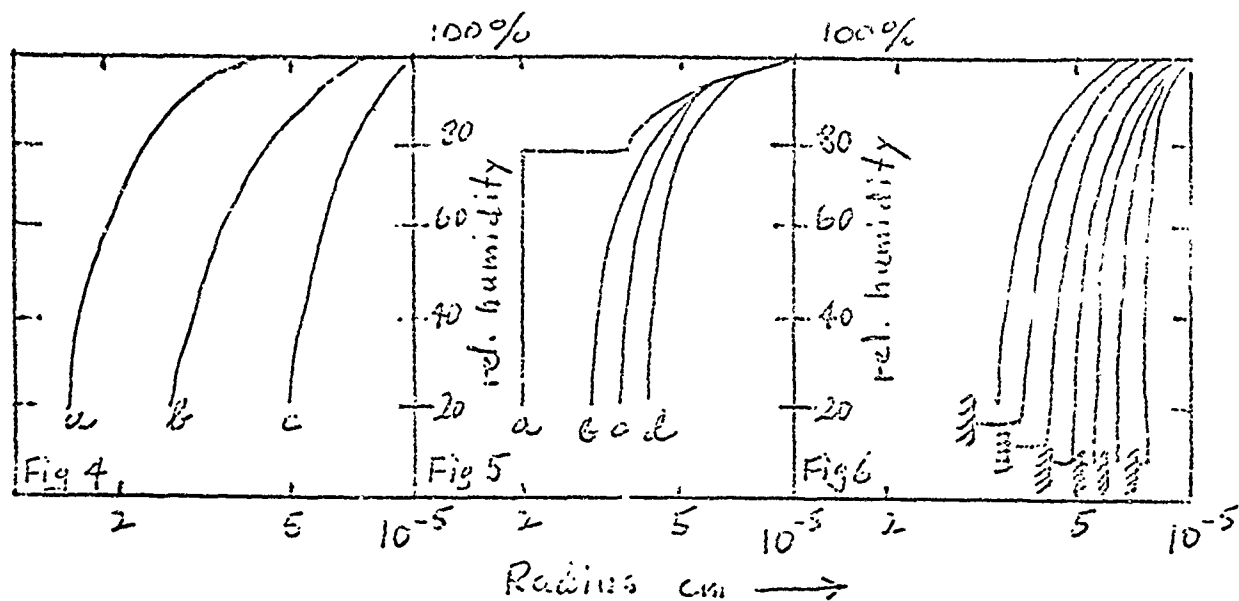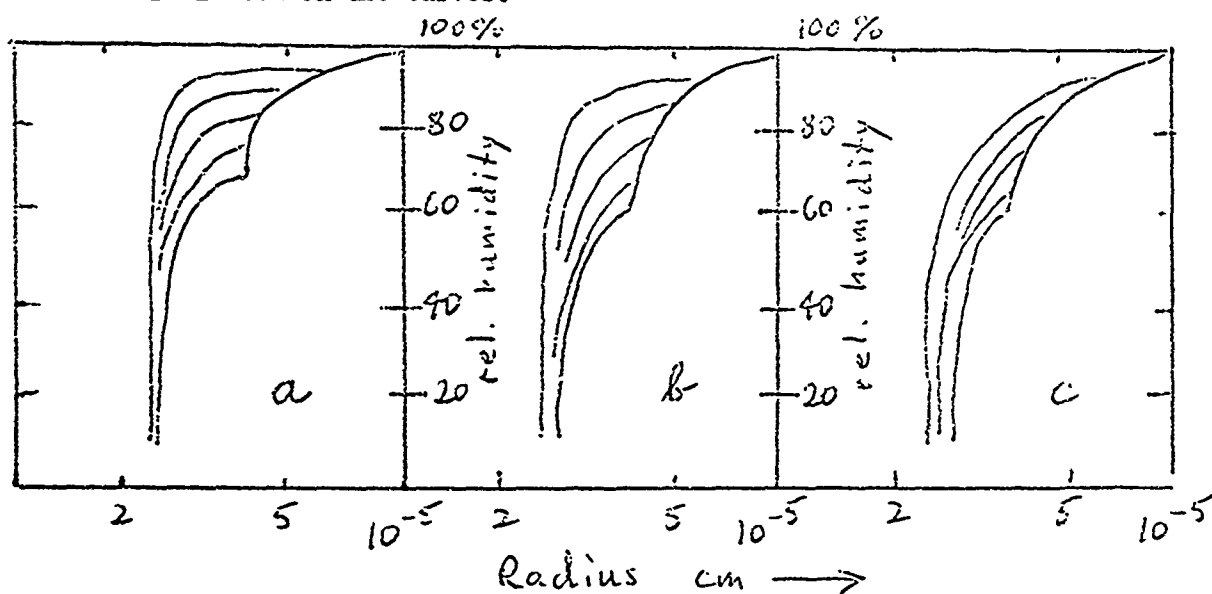
Fig. 4. Growth curves of HNO_3 at different potential radii ($10^\circ C$)
Potential radius at: $a = 10^{-4}$ cm, $b = 10^{-5}$ cm, $c = 10^{-6}$ cm.

Fig. 5. Growth curves of different substances at a potential
radius of 10^{-5} cm. a: NaCl $10^\circ C$, b: HNO_3 $10^\circ C$, c: $CaCl_2$ $25^\circ C$,
d: H_2SO_4 $10^\circ C$.

Fig. 6. Growth curves of mixed nuclei with insoluble nucleus at
a potential radius of 10^{-5} cm for H_2SO_4. The size of the solid radius
is indicated on the curves.

Fig. 7. Growth curves of mixed nuclei, the solid nucleus of which possesses diverse solubility.
a) volume ratio droplet:solid nucleus at 40% humidity about 1.5
b)   "   2.0
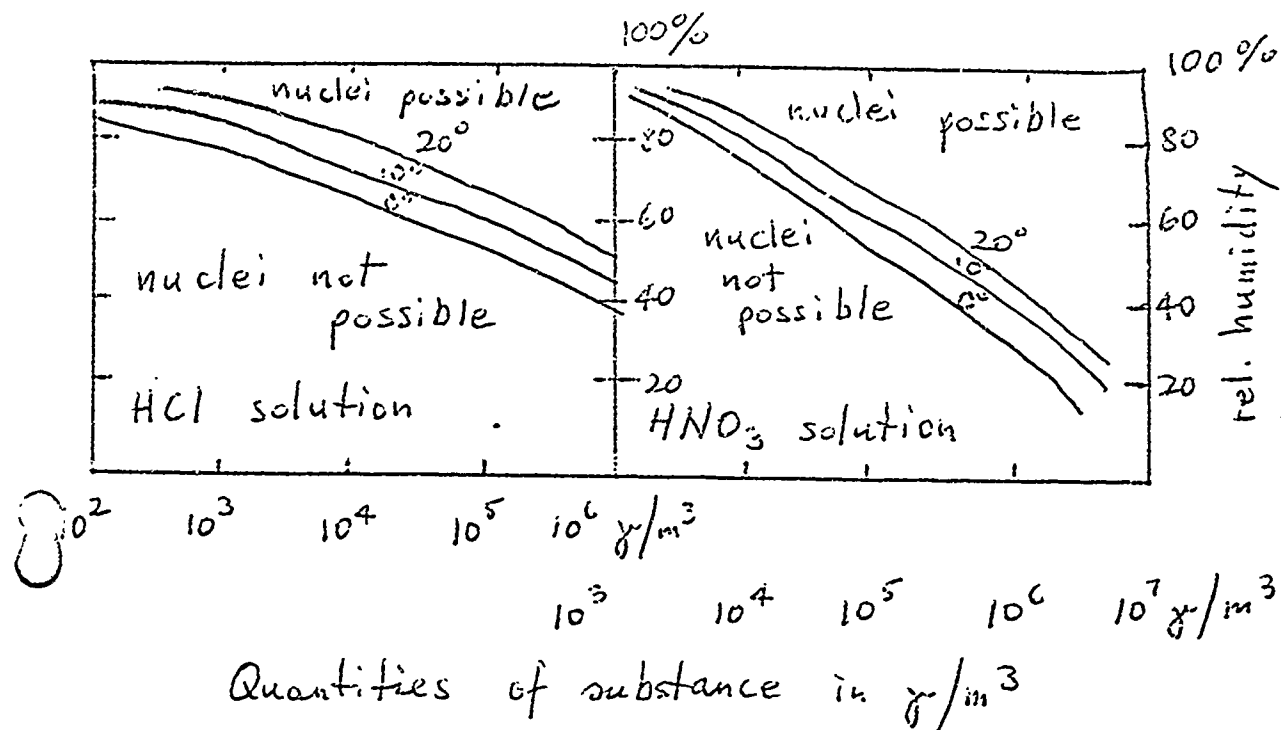c)   "   4.0

Fig. 8. Existence capability of solutional droplets of poorly volatile substances depending on relative humidity and amount of material per cbm air at different temperatures. The lines demarcate the area in which such pure solutional nuclei are possible.

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